

PROCESS AND CATALYSTS FOR THE PRODUCTION OF LINEAR ALKANES

The present invention relates to a process for the production of linear alkanes containing less than 6 carbon atoms, which comprises putting a mix including one or more hydrocarbons containing at least 6 carbon atoms, in contact with a suitable catalytic composition containing one or more metals and a Y-type zeolite.

The mixtures which can be used for the process of the present invention are, for example, mixtures comprising one or more C₆₊ hydrocarbons selected from alkanes, alkenes with one or more unsaturations, aromatic compounds. In particular, these mixtures can be fractions from mineral oil, fractions from catalytic or thermo conversion plants, and fractions deriving therefrom by hydrogenation.

Mixtures of hydrocarbons rich in aromatic components are very common in the petrochemical industry: for example, those deriving from the steam-cracking of virgin naphtha to olefins, or those obtained from the reforming of petroleum fractions, can be mentioned.

Low molecular weight aromatic compounds (< 9 carbon atoms) which can be obtained from these mixtures, are widely used as chemical intermediates and as components of motor-vehicle fuels. The use of medium molecular

weight (up to 12 carbon atoms) components of these mixtures as chemical intermediates and in fuels is more restrained, but still economically important. The use of higher molecular weight components is less advantageous 5 and their main destination is as a low-price fuel.

The percentage of aromatic compounds which are used as fuel components is inevitably decreasing. The legislation in Europe, as well as in other parts of the world, is in fact tending to progressively decrease the aromatic 10 content in fuel, for environmental reasons, and there will therefore be an excess production of aromatic products with 7 and 8 carbon atoms, which will not easily find alternative uses in the chemical field and a significant loss in the value of these fractions is expected 15 in a reasonably near future.

Higher molecular weight fractions already have a current low market value, in fact, with the rare exceptions of mixtures with a moderate content of asphaltenes, they are at the same price level as fuel oil.

20 In particular, mixtures containing hydrocarbons with a different chemical structure for which the necessity is presently felt for finding alternative means of exploitation, are those deriving from so-called cracking gasolines and reforming residues. These hydrocarbon fractions 25 derive from cracking gasolines (also called pyrolysis

gasoline or pygas) or from reforming gasoline after the more valuable components, such as benzene, toluene and xylenes, have been at least partially separated from them. Cracking/reforming gasolina residue does not have a 5 fixed composition, also because mixtures of a different origin can be joined in varying proportions. From the point of view of the components, it should be pointed out that benzene, toluene and xylenes are still present in these mixtures, as the previous separation process is 10 never total, the main components present are aliphatic hydrocarbons with varying structures having 7-9 carbon atoms, ethyl benzene and other alkyl benzenes with 9-12 carbon atoms, styrene and methyl styrenes, methyl cyclopentadiene, dicyclopentadiene and various co-dimers 15 of cyclopentadiene and methyl cyclopentadiene starting from 9 carbon atoms (for example in the case of the co-dimer between cyclopentadiene and butadiene) up to 15 carbon atoms (for example in the case of co-dimers between methyl styrene and methyl cyclopentadiene), indene 20 and methyl indenes, naphthalene and methyl naphthalenes. In mixtures of this type there are therefore carbon-carbon bonds prevalently of the aromatic type, but bonds of the aliphatic, olefinic and dienic type are present, prevalently with cyclic structures.

25 Fractions containing alkanes and/or alkenes with one

or more unsaturations for which the necessity is felt for finding alternative means of exploitation, can directly derive from the fractionation of crude mineral oil, but for the purposes of the present invention, mixtures deriving from other processings and which, being by-products, have a low commercial value, are considered as being preferential. Mixtures of hydrocarbons of particular interest are those which do not require any further preliminary intervention of a chemical or physico-chemical nature, for example residual paraffinic waxes from the dewaxing treatment of lubricants, mixtures, however, obtained with known treatments, which are relatively simple and with a wide application, can also be well used, such as for example naphthene fractions deriving from the hydrogenation of aromatic hydrocarbon mixtures.

With respect to the possible exploitation of various hydrocarbon cuts described above, conversion processes of mineral oil fractions comprising cyclic and aromatic alkanes to non-cyclic branched alkanes, are known in the state of the art.

US 5,831,139, for example, describes a process for the production of aliphatic fuels from naphtha with a high boiling point. The naphtha is subjected to hydrogenation, in a first step, to transform the aromatic com-

pounds into cyclic alkanes. After the hydrogenation, the synthesis of isoparaffins is effected in a second phase. Aliphatic gasoline components are produced with this process by the opening of the ring and the synthesis of 5 isoparaffins, with as many branchings as possible, without a decrease in the number of carbon atoms with respect to the hydrocarbons charged. The octane number of the product must in fact be high.

US 5,334,792, as in the above patent US 5,831,139, 10 describes a process for the opening of the ring for aromatic and cyclo-aliphatic compounds. This opening step is followed by an isomerization step. Also in this case, iso-alkanes are produced without a reduction in the number of carbon atoms with respect to the starting hydro- 15 carbons.

The conversion, by means of ring opening, of fractions containing naphthenes in diesel fuels, is also known. A process of this type is described, for example, in WO 97/09288. Also in this case, alkanes are produced 20 without a decrease in the number of carbon atoms with respect to the hydrocarbons charged. The cetane number of the product must be as high as possible.

The processes of the known art therefore aim at transforming aromatic or cyclo-aliphatic compounds into 25 iso-alkanes or alkanes with a high number of carbon at-

oms, suitable for diesel fuels, i.e. the transformations take place without a substantial variation in the number of carbon atoms.

An object of the present invention relates to a 5 process which allows hydrocarbons mixtures deriving from mineral oil, to be transformed by means of a catalyzed hydrocracking reaction, into linear alkanes with a lower molecular weight, in particular linear alkanes containing less than 6 carbon atoms, which are an excellent charge 10 for steam-cracking plants.

WO 01/27223 claims, for this purpose, the use of zeolites with a Spaciousness Index (S.I.) lower than 20, exchanged with hydrogenating metals. The preferred zeolite is ZSM-5 exchanged with palladium.

15 Using this catalyst, the complete conversion of model charges (toluene, cyclo-hexane or pseudo-cumene) is obtained with a distribution of the reaction products ranging from methane to butanes. Approximately 5% of methane is formed among the alkanes, which is a compound 20 that in the subsequent steam-cracking treatment of the mixture obtained with the process indicated, does not give any yield to olefins. In WO 01/27223, it is demonstrated that large pore zeolites, such as Y-zeolite (S.I. = 21) cannot be used in this reaction as their catalytic 25 activity rapidly declines. After only 8 hours of life,

using Y-zeolite in acidic form, the conversion, in fact, passes from 100% to 74%. The life of ZSM-5 zeolite/Pd, on the contrary, is at least 10 hours.

Italian patent application MI2003A000347 describes a 5 process for the conversion of mixtures containing aromatic compounds in linear alkanes which uses a catalytic composition containing at least one lanthanide, at least one metal of group VIII and a Y-type zeolite.

It has now been found that by using catalytic compositions 10 containing a Y-type zeolite in a mixture with suitable elements, it is possible to produce linear alkanes with a low molecular weight, in particular linear alkanes containing less than 6 carbon atoms, from mixtures comprising one or more hydrocarbons whose structure 15 contains at least 6 carbon atoms.

An object of the present invention therefore relates to a process for the production of linear alkanes containing less than 6 carbon atoms which comprises putting a mixture comprising one or more hydrocarbons containing 20 at least 6 carbon atoms, in contact with a catalytic composition comprising:

- a) at least an element Me selected from Zn, Mo, Cu, Ga, In, W, Ta, Zr, Ti, metals of group VIII Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt,
- 25 b) a zeolite selected from Y-zeolite and Y-zeolite modi-

fied by partial or total substitution of the Si with Ti or Ge and/or partial or total substitution of the aluminum with Fe, Ga or B,
with the exclusion of a catalytic composition comprising
5 at least one lanthanide, at least one metal belonging to group VIII and a zeolite selected from Y-zeolite and Y-zeolite modified by partial or total substitution of the Si with Ti or Ge and/or partial or total substitution of the aluminum with Fe, Ga or B when the mixture treated is
10 a mixture containing aromatic compounds.

The process of the present invention allows n-alkanes to be obtained, with a lower number of carbon atoms than that of the hydrocarbon fed. In particular, prevalently linear alkanes containing from 2 to 5 carbon
15 atoms, are obtained.

Various kinds of hydrocarbon charge can be used and the resulting products form an excellent feed for steam-cracking plants, where they undergo transformation into olefins, mainly ethylene and propylene. With these catalytic compositions optimum results are obtained in terms
20 of activity and catalytic life.

The mixtures which can be subjected to the process of the present invention are mixtures comprising one or more hydrocarbons, whose structure contains at least 6
25 carbon atoms, selected from aromatic compounds, alkanes

or alkenes with one or more unsaturations. The aromatic compounds can contain several condensed benzene rings.

Mixtures containing aromatic compounds or mixtures containing one or more alkanes with open chains or cyclic 5 structures and/or alkenes having one or more unsaturations with open-chains or cyclic structures, optionally mixed with aromatic compounds, are preferably used.

For mixtures containing aromatics, catalytic compositions are used, comprising:

10 (a) at least an element Me selected from Zn, Mo, Cu, Ga, In, W, Ta, Zr, Ti, metals belonging to group VIII,
(b) a zeolite selected from Y-zeolite and Y-zeolite modified by partial or total substitution of the Si with Ti or Ge and/or partial or total substitution of the aluminum with Fe, Ga or B,
15 with the exclusion of a catalytic composition comprising at least one lanthanide, at least one metal belonging to group VIII and a zeolite selected from Y-zeolite and modified Y-zeolite.

20 Modified Y-zeolite always refers in this description to a Y-zeolite modified by partial or total substitution of the Si with Ti or Ge and/or partial or total substitution of the aluminum with Fe, Ga or B.

In particular, the mixtures containing aromatic compounds 25 can be treated with catalytic compositions which

essentially consist of:

- (a) at least an element Me selected from Zn, Mo, Cu, Ga, In, W, Ta, Zr, Ti, metals belonging to group VIII,
- (b) a zeolite selected from Y-zeolite and modified Y-
5 zeolite.

According to an aspect of the invention, catalytic compositions additionally containing one or more lanthanides, can be used.

A further aspect of the present invention therefore 10 relates to a process for the production of linear alkanes containing less than 6 carbon atoms which comprises putting a mixture comprising one or more hydrocarbons containing at least 6 carbon atoms, in contact with a catalytic composition comprising:

- 15 a) at least an element Me selected from Zn, Mo, Cu, Ga, In, W, Ta, Zr, Ti, metals of group VIII, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt,
- b) a zeolite selected from Y-zeolite and Y-zeolite modified by partial or total substitution of the Si with Ti
20 or Ge and/or partial or total substitution of the aluminum with Fe, Ga or B,
- c) one or more lanthanides,

with the exclusion of a catalytic composition comprising at least one lanthanide, at least one metal belonging to
25 group VIII and a zeolite selected from Y-zeolite and

modified Y-zeolite when the mixture treated is a mixture containing aromatic compounds.

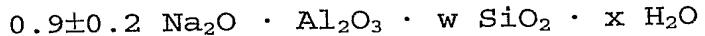
In the case of mixtures containing aromatic compounds, compositions can be well used, containing:

- 5 a) at least an element Me selected from Zn, Mo, Cu, Ga, In, W, Ta, Zr, Ti,
- b) a zeolite selected from Y-zeolite and Y-zeolite modified by partial or total substitution of the Si with Ti or Ge and/or partial or total substitution of the aluminum with Fe, Ga or B,
- 10 c) one or more lanthanides,
 with the exclusion of a catalytic composition comprising at least one lanthanide, at least one metal belonging to group VIII and a zeolite selected from Y-zeolite and
- 15 modified Y-zeolite.

In particular, mixtures containing aromatic compounds can be converted using catalytic compositions essentially consisting of:

- 20 a) at least an element Me selected from Zn, Mo, Cu, Ga, In, W, Ta, Zr, Ti,
- b) a zeolite selected from Y-zeolite and Y-zeolite modified by partial or total substitution of the Si with Ti or Ge and/or partial or total substitution of the aluminum with Fe, Ga or B,
- 25 c) one or more lanthanides.

Y-zeolite is described for the first time in US 3,130,007 and has the following formula expressed in terms of moles of oxides



5 wherein w has a value greater than 3 up to about 6 and x can be a value up to about 9. Its preparation is described for example in "Verified Synthesis of Zeolitic materials" H. Robson Editor, Elsevier, second revised edition 2001, whereas the post-synthesis treatment to 10 which the Y-zeolite can be subjected, including dealumination, is described in "Introduction to Zeolite Science and Practice" chapter 5, H. van Bekkum et al. Editors, Studies in Surface Science and Catalysis, vol. 58, Elsevier. In the compositions of the present invention, Y-15 zeolites can be used with a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranging from 3 to 400.

Modifications of the Y-zeolite obtained by partial or total isomorphous substitution of the aluminum of the zeolite with Fe, Ga or B, and/or partial or total substitution of the Si with Ti or Ge, can also be used in the process of the present invention. These modifications of the Y-zeolite can be prepared, for example, by substituting, in the synthesis process of the Y-zeolite described in US 3,130,007, part of the silicon and/or aluminum 20 sources with sources of Fe, Ga, B, Ti and/or Ge. The Y-25

zeolite in which Ge has totally substituted the Si is described in R.M. Barrer et al. J. Chem. Soc., 195-208 (1959) and in G.M. Johnson, Microporous and Mesoporous Material, 31, 195-204 (1999); the Y-zeolite in which the 5 Si and Al have been completely substituted by Ge and Ga are described in Barrer, J. Chem. Soc., 195-208 (1959).

The catalytic composition of the present invention preferably contains the zeolite in partially acidic form, that is part of the cationic sites present in the zeolite 10 is occupied by hydrogen ions.

A particularly preferred aspect is to use Y-zeolite. In the Y-zeolite, the molar ratio between silicon oxide and aluminum oxide preferably ranges from 5 to 50. .

With respect to the element Me, compositions containing 15 Pt, Pd, Ti, Mo, Zn, Cu or Ni, are preferably used. Among the metals of group VIII, Pd is preferably adopted. The mixtures of elements preferably used are selected from Pd/Ti, Zn/Mo, Cu/Zn and Ni/Mo.

The element Me can be present in the catalytic composition 20 in the form of an oxide, ion, metal, sulfide or a mixture of these forms can be present. In particular, the elements Zn, Mo, Cu, Ga, In, W, Ta, Zr, Ti, are prevalently present in the form of oxides, the elements of group VIII are prevalently present in the metal form.

25 When Me is an element selected from Zn, Mo, Cu, Ga,

In, W, Ta, Zr, Ti, the quantity of Me, expressed as an element, can vary from 0.1 to 50% by weight, preferably from 0.5 to 30% by weight, with respect to the total weight of the catalytic composition.

5 When Me is an element selected from metals of group VIII, the quantity of Me, expressed as an element, can vary from 0.001 to 10% by weight, preferably from 0.1 to 5% by weight with respect to the total weight of the catalytic composition.

10 When present, the element belonging to the group of lanthanides which is preferably used is lanthanum.

The lanthanide, or lanthanides, present in the catalytic composition can be in the form of an oxide or ion or a mixture of these forms can be present. The quantity 15 of lanthanide, or lanthanides, expressed as an element, can vary from 0.5 to 20% by weight, preferably from 1 to 15% by weight, with respect to the total weight of the catalytic composition.

The catalytic compositions of the present invention 20 are prepared by introducing the element Me by means of the ionic exchange or impregnation techniques.

If the element Me is introduced by ion exchange, the zeolite, preferably in acidic form, is treated with an aqueous solution of a salt of the element Me. For example, in the case of metals of group VIII, an aqueous so- 25

lution can be used with a concentration of 0.01-0.5 M, preferably 0.01-0.1 M, of a corresponding complex. For palladium, $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$, can be used, for example.

The sample deriving from the ion exchange, is dried, 5 after suitable washings, and then calcined at a temperature ranging from 400 to 600°C for 1-10 hours.

If the element Me is introduced by impregnation, the known incipient wetness inbibition technique (wet imbibition) is adopted, wherein the volume of solution containing a salt of the element Me corresponds to the pore volume of the zeolite, it is then dried and calcined as in the case of the ion exchange. Also in this case, an aqueous solution of a salt of the element Me is used, preferably with an anion which does not leave residues in the 15 end-product, for example a nitrate or an acetate decomposable by calcination. When the quantity of the element Me to be introduced is high, the salt to be added is divided and various impregnations are effected, with drying phases in between. The drying is carried out by heating 20 the sample and, in order to facilitate the evaporation of the solvent, vacuum or a stream of gas can be optionally used.

As a result of the calcination, an at least partial transformation of the ion of the element Me into the corresponding oxide, can take place. 25

Impregnation is the preferred technique for introducing the element Me.

In catalytic compositions in which the introduction of more than one element Me selected from Zn, Mo, Cu, Ga, 5 In, W, Ta, Zr, Ti and metals of group VIII on the zeolite, preferably in acidic form, is required, the elements can be introduced separately or contemporaneously. In the former case, the calcination between the introduction step of a first element and the introduction step of 10 a second element is optional; if this calcination is not effected, the partial transformation of the ions into the corresponding oxides, takes place contemporaneously during the calcination effected at the end of the second step.

15 According to the preferred technique, the introduction of several elements is effected contemporaneously and for this purpose, aqueous solutions containing said elements in the desired atomic ratio, are used.

When the catalytic composition envisages the introduction 20 of a lanthanide, any of the known techniques can be used, such as exchange in the solid state with a lanthanide salt, ion exchange in aqueous solution or impregnation.

Ion exchange or impregnation is preferably used. 25 In the former case, the zeolite, preferably in

acidic or ammonium form, is treated with an aqueous solution of a lanthanum salt having a concentration varying from 0.01 to 1.0 M, preferably from 0.01 to 0.5 M. For example, an aqueous solution can be used, within the concentration limits indicated above of lanthanum nitrate, citrate, acetate, chloride or sulfate, at reflux temperature for 1-24 hours. After suitable washings with distilled water, the sample deriving from the ion exchange is dried and then calcined at a temperature ranging from 400 to 600°C for 1-10 hours.

If the lanthanide is introduced by impregnation, the incipient wetness imbibition technique is used and it is then dried and calcined as in the case of ion exchange.

As a result of the calcination, an at least partial transformation of the lanthanide ion into the corresponding oxide, takes place.

Ion exchange is the preferred technique for introducing the lanthanide.

The catalytic compositions of the present invention containing one or more lanthanides and one or more elements Me can be prepared using a mixture of compounds of these elements and any of the techniques described above.

These catalytic compositions are preferably prepared by introducing first the lanthanide and then the element Me onto the zeolite. The zeolite used in the preparation

is preferably in acidic form. When these catalytic compositions contain one or more lanthanide or more than one element Me, a mixture of compounds of these elements is used in their preparation.

5 According to a particularly preferred aspect, the catalytic compositions of the present invention containing lanthanum are prepared by inserting the lanthanide in the zeolite in acidic form by means of ion exchange, optionally calcining the product thus obtained, and then 10 depositing the element Me by ion exchange and calcining the product obtained.

Whatever technique may have been selected for introducing the lanthanide and element Me, the calcination between the introduction of the lanthanide and the introduction of the element Me is generally optional and if it 15 is not effected, the partial transformation of the ions into the corresponding oxides takes place contemporaneously during the calcination effected at the end of the second step.

20 Catalytic compositions containing or consisting of Y-zeolite and Pd, Y-zeolite and Pt, Y-zeolite and Zn, Y-zeolite and Mo, Y-zeolite and Ni; Y-zeolite and Pd together with Ti, Y-zeolite and Zn together with Mo, Y-zeolite and Zn together with Cu, Y-zeolite and Mo together with Ni, Y-zeolite and La together with Zn and Mo, 25

y-zeolite and La together with Zn and Cu, are particularly preferred.

When the catalytic composition contains elements of group VIII, following the synthesis step, there may be an 5 at least partial reduction step of the relative ions to the corresponding elements. Reduction to the element can be obtained by means of treatment of the catalytic composition with hydrogen or with a reducing agent, and it can be effected on the catalytic composition before its use 10 or in the reactor itself in which the catalytic composition is used.

The catalytic composition of the present invention can be used in a mixture with suitable binders such as silica, alumina, clay. The catalytic composition and the 15 binder are mixed in a proportion ranging from 5:95 to 95:5, preferably from 30:70 to 95:5, even more preferably from 50:50 to 90:10. The mixture of the two components is processed, according to the known techniques, into the desired end-form, for example cylindrical extruded products 20 or other known forms.

The mixtures containing aromatic compounds which are suitable for being treated according to the process of the present invention, are for example fractions coming from thermal or catalytic conversion plants, and mineral 25 oil fractions rich in aromatic compounds, such as for ex-

ample pyrolysis gasolines or pygas, fractions coming from pyrolysis gasolines, in particular those from which the light aromatic compounds (from 6 to 8 carbon atoms) have been separated and residual fractions with a low commercial value coming from production plants of aromatic compounds and reforming.

In particular, pyrolysis gasolines are a by-product of steam cracking processes in which ethylene and propylene are obtained from light hydrocarbon cuts such as straight-run naphtha (oil fraction substantially containing C₅ and C₆ hydrocarbons), LPG (Liquefied Petroleum Gas, an oil fraction containing C₃ and C₄ hydrocarbons), propane or ethane.

Mixtures containing one or more alkanes with open chains or with cyclic structures and/or alkenes having one or more unsaturations with open chains or cyclic structures, which are suitable for being treated according to the process of the present invention, are those deriving from the fractionation of crude mineral oil or from the hydrogenation of mineral oil fractions or the hydrogenation of cracking plant fractions.

The hydrogenation of these fractions can be carried out with any of the known methods and catalysts, such as, for example, those based on Ni carried on alumina. The fractions deriving from this treatment prevalently or

completely contain alkane compounds with a cyclic structure.

The charges suitable for being treated with the process of the present invention can be optionally mixed 5 with heavier fractions, coming for example from fuel oil from steam cracking (FOK) or Light Cycle Oil (LCO) from fluid bed catalytic cracking. These heavy fractions contain polycyclic aromatic compounds having up to 20-21 carbon atoms. As these heavy fractions also contain sulfur, which is known to be poisonous for hydrogenation catalysts, an unexpected and extremely advantageous aspect is that the catalytic compositions of the present invention do not, on the contrary, undergo any deactivation due to the sulfur and are therefore capable of processing 10 mixtures of aromatic hydrocarbons also containing heavier fractions, such as, for example, FOK and LCO. During the treatment of these mixtures, there may be an at least partial transformation of the elements Me contained 15 in the catalytic composition used, for example Mo, Zn, Cu, into the corresponding sulfides. As already mentioned, this transformation does not seem to invalidate 20 the activity of the catalytic composition.

The dilution of very heavy mixtures (FOK, LCO) with lighter fractions is not indispensable. Another unexpected 25 aspect of the present invention relates to the

processing of heavier fractions, coming, for example, from fuel oil from steam cracking (FOK) or Light Cycle Oil (LCO) from fluid bed catalytic cracking, also without dilution with fractions coming from gasolines, provided a 5 process is effected which avoids feeding heavier polycyclic components such as asphaltenes, to the conversion reactor to light paraffins. For this purpose, the fuel oil fraction can be subjected to treatment such as extraction with a solvent, distillation or, even better, 10 evaporation with suitable equipment (Luwa thin film evaporator or similar equipment).

US 5,932,090 describes, for example, a process for the conversion of heavy crude oils or distillation residues which, after a hydrocracking phase in the presence 15 of hydrogen and a suitable catalyst, comprises distillation of the product to recover the most volatile hydrocarbons. By deasphalting the distillation residue, a mixture of hydrocarbons is obtained (called DAO, deasphalting oil), from which a feed can be obtained, which is suitable 20 for the process of the present invention.

Also in these cases, the catalytic compositions of the present invention unexpectedly do not undergo any deactivation due to the sulfur which can be contained in these mixtures and there can be an at least partial 25 transformation of the elements Me contained in the cata-

lytic composition used into the corresponding sulfides without a loss in the catalytic activity.

The mixtures containing aromatic compounds which can be subjected to the process of the present invention, and 5 in particular pyrolysis gasolines, generally prevalently contain toluene, ethyl benzene, xylenes, benzene and C₉ aromatic compounds, but also naphthalene and alkyl derivatives of naphthalene, for example mono and poly-substituted methyl and ethyl derivatives. The intermediate fractions and fuel oils such as FOK and LCO can contain aromatic compounds with >20 carbon atoms, such as, for example, aromatic compounds with 2-4 condensed benzene rings, naphthalene, phenanthrene, anthracene, benzanthracene, with the relative alkyl derivatives (in particular methyl and/or ethyl derivatives) and phenyl derivatives, indene, biphenyl, fluorene, binaphthyl.

According to an aspect of the present invention, the resulting fraction of n-alkanes is prevalently made up of ethane, propane, n-butane and n-pentane.

20 According to a preferred aspect of the present invention, the fraction of linear alkanes containing from 2 to 5 carbon atoms ranges from 50 to 90% by weight of the resulting product.

25 The process of the present invention is carried out in the presence of hydrogen or a mixture of hydrogen and

H_2S at a pressure ranging from 5 to 200 bar, preferably from 25 to 100 bar, at a temperature ranging from 200°C to 700°C, preferably from 300° to 600°C. A weight ratio H_2/charge ranging from 0.1 to 1.4, more preferably from 5 0.1 to 0.7, is preferably adopted.

According to a particular aspect of the invention, it is possible to operate with the use, in addition to hydrogen, of a diluent, and for this purpose, a paraffin, for example methane or ethane, can be used.

10 A particular advantageous aspect of the present invention relates to the possibility of using hydrogen or a diluent containing H_2S impurities. As specified above, the catalysts used in the present invention are not generally sensitive to the presence of sulfur.

15 The process is preferably carried out in continuous, in a fixed bed or fluid bed reactor, in gaseous or partially liquid phase, at a WHSV (Weight Hourly Space Velocity, expressed in kg of charge/hour/kg of catalyst) ranging from 0.1 to 20 hours⁻¹, preferably from 0.2 to 5 20 hours⁻¹, even more preferably from 0.5 to 3 hours⁻¹.

The alkenes with one or more unsaturations present in the feed are converted according to the process described in the present invention analogously to the other hydrocarbons, both alkanes and aromatic compounds. It has 25 been verified however that the presence of compounds of

this type can, in some cases, facilitate the formation of oligomers/polymers under the conditions in which the process, object of the invention, is carried out, and it may therefore be preferable to previously subject the 5 mixtures containing them to hydrogenation in order to prolong the duration of the industrial run, without frequent stoppages and intermediate regenerations of the catalytic bed. The preliminary hydrogenating treatment can be carried out at a low temperature, in liquid phase, 10 according to technologies already known, for example applied to the fractions of hydrocarbons destined for use as fuel for motor vehicles; this is generally light hydrogenating treatment normally but not exclusively effected with Pd-based catalysts on alumina.

15 Before use, the catalytic composition of the present invention is preferably activated in nitrogen at a temperature ranging from 300 to 700°C, for a time ranging from 1 to 24 hours and at a pressure varying from 0 to 10 barg.

20 In addition to or in substitution of the above, in particular when elements of group VIII are present, an activation with hydrogen can be effected at a temperature of 300-700°C, a pressure of 0-10 barg, for a time ranging from 1 to 24 hours.

25 The catalyst allows long operating periods before

showing signs of deactivation; the catalyst however can be subjected to regeneration treatment, re-establishing its original performances. The most suitable method is by the combustion of the carbonaceous deposits accumulated 5 in the operating period, according to what is known in the state of the art, operating, for example, at a temperature ranging from 450 to 550°C, at a pressure ranging from 1 to 3 bar, with mixtures of oxygen and nitrogen in a ratio ranging from 0.1 to 20% by volume and with a 10 space velocity (GHSV = Gas Hourly Space Velocity, expressed in l of gas mixture/hour/l of catalyst) ranging from 3000 to 6000 hours⁻¹. Considering the low regeneration frequency, it is not necessary for the regeneration to be effected in the same reactor in which the catalyst 15 is introduced for the reaction; the catalyst can be discharged during the periodic plant maintenance phases and regenerated elsewhere, in this way the reactor can be constructed without control devices necessary for carrying out the regeneration.

20 The catalytic compositions used in the present invention are new and a further object of the present invention therefore relates to a catalytic composition comprising:

(a) at least one element Me selected from Zn, Mo, Cu, Ga, 25 In, W, Ta, Zr, Ti and metals of group VIII Fe, Co, Ni,

Ru, Rh, Pd, Os, Ir, Pt,

(b) a zeolite selected from Y-zeolite and Y-zeolite modified by partial or total substitution of the Si with Ti or Ge and/or partial or total substitution of the aluminum with Fe, Ga or B,

5 with the exclusion of catalytic compositions comprising at least one lanthanide, at least one metal belonging to group VIII and a zeolite selected from Y-zeolite and modified Y-zeolite.

10 These compositions can additionally contain one or more lanthanides.

An object of the present invention also relates to a process for the production of linear alkanes containing less than 6 carbon atoms from mixtures containing aromatic compounds having a structure with at least 6 carbon atoms using a catalytic composition essentially consisting of:

(a) at least one element Me selected from Zn, Mo, Cu, Ga, In, W, Ta, Zr, Ti in a mixture with one or more metals of 20 group VIII,

(b) a zeolite selected from Y-zeolite and Y-zeolite modified by partial or total substitution of the Si with Ti or Ge and/or partial or total substitution of the aluminum with Fe, Ga or B,

25 c) one or more lanthanides.

The catalytic compositions used in said process are also new and object of the present invention. Some illustrative but non-limiting examples are provided for a better understanding of the present invention and 5 for its embodiment, but should in no way be considered as limiting the scope of the invention itself.

EXAMPLES OF CATALYST PREPARATION

EXAMPLE 1

20 g of Y-zeolite in commercial extruded acidic form 10 (Zeolyst CBV500 CY (1.6)) with a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 5.2, and a solution consisting of 160 ml of water and 11.2 g of an aqueous solution of tetra-amine palladium nitrate (Pd 5% max., Alfa Aesar), are charged into 15 a glass flask. The solution is stirred for 4 hours at room temperature; at the end of this period, it is filtered on a Buckner funnel, washed and dried in an oven at 120°C for 16 hours. Calcination is effected at a temperature of 400°C in air, for 12 hours. A Y-zeolite is obtained, containing 2.1% by weight of Pd.

20 The material is crushed to granules within the 20-40 mesh range.

EXAMPLE 2

30 g of the same Y-zeolite used in Example 1 are charged into a glass flask. A solution is prepared, using 25 4.6 g of ammonium heptamolybdate, 5.2 g of hexahydrated

zinc nitrate and 62.4 g of demineralized water. The extruded zeolite is impregnated using the incipient wetness imbibition technique, with a third of the previous solution, dried at 120°C, impregnated again with a third of the solution, dried again, further impregnated with the remaining volume of the solution, dried and then calcined at 500°C for 4 hours.

A catalyst is obtained with 7.0% by weight of Mo and 3.2% by weight of Zn.

The material is crushed to granules within the 20-40 mesh range.

EXAMPLE 3

30 g of the same Y-zeolite used in Example 1 are charged into a glass flask. A solution is prepared, using 6.08 g of tri-hydrated copper nitrate, 4.76 g of hexahydrated zinc nitrate and 62.4 g of demineralized water. The extruded zeolite is impregnated using the incipient wetness imbibition technique, with a third of the previous solution, dried at 120°C, impregnated again with a third of the solution, dried again, further impregnated with the remaining volume of the solution, dried and then calcined at 500°C for 4 hours.

A catalyst is obtained with 4.8% by weight of Cu and 3.1% by weight of Zn.

The material is crushed to granules within the 20-40

mesh range.

EXAMPLE 4

30 g of the same Y-zeolite used in Example 1 are charged into a glass flask. A solution is prepared using 5 2.316 g of ammonium heptamolybdate and 62.4 g of demineralized water. The extruded zeolite is impregnated using the incipient wetness imbibition technique, with a third of the previous solution, dried at 120°C, impregnated again with a third of the solution, dried again, further 10 impregnated with the remaining volume of the solution, dried and then calcined at 500°C for 4 hours.

A catalyst is obtained with 4.0% by weight of Mo.

The material is crushed to granules within the 20-40 mesh range.

15 EXAMPLE 5

30 g of the same Y-zeolite used in Example 1 are charged into a glass flask. A solution is prepared, using 2.72 g of hexa-hydrated zinc nitrate and 30 g of demineralized water. The extruded zeolite is impregnated using 20 the incipient wetness imbibition technique, with a third of the previous solution, dried at 120°C, impregnated again with a third of the solution, dried again, further impregnated with the remaining volume of the solution, dried and then calcined at 500°C for 4 hours.

25 A catalyst is obtained with 1.9% by weight of Zn.

The material is crushed to granules within the 20-40 mesh range.

EXAMPLE 6

75 g of commercial Y-zeolite (Tosoh HSZ 320 HOA) with a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 5.5 and a sodium content, as Na_2O oxide, of 4% by weight, and 1500 g of a 2 molar aqueous solution of ammonium nitrate, are charged into a 2 liter glass flask. The suspension is maintained under reflux conditions for 3 hours, under stirring; after this period, it is filtered on a Buckner vacuum funnel, is dried in an oven and calcined at a temperature of 550°C in air, for 5 hours, obtaining a Y-zeolite in acidic form. 20 g of the solid product thus obtained are exchanged with a solution consisting of 160 ml of water and 11.2 g of an aqueous solution of tetra-amine palladium nitrate (Pd 5% max., Alfa Aesar). The mixture is stirred for 4 hours, at room temperature. After this period, it is filtered on a Buckner funnel, washed and dried in an oven at 120°C for 16 hours. Calcination is effected at a temperature of 400°C in air for 12 hours. 16 g of the catalyst thus obtained are mixed with 10.81 g of pseudoboehmite VERSAL 250 (UOP) and 64 g of an aqueous solution of acetic acid at 1.5%. The whole mixture is stirred for 30 minutes at room temperature, and is then dried on a heated plate. It is subsequently dried at

120°C for 16 hours and is calcined at 500°C for 4 hours.

A Y-zeolite is obtained, containing 1.5% by weight of Pd, bound with alumina, wherein the amount of binder corresponds to about 30% of the total weight of the catalytic composition.

5 The material is crushed to granules within the 20-40 mesh range.

EXAMPLE 7

25 g of the same Y-zeolite used in Example 1 are 10 treated with a solution containing 43.3 g of hexahydrated lanthanum nitrate in 500 g of demineralized water. The solution is maintained under reflux conditions for 3 hours under stirring. At the end of this period, the solution is filtered, the filtrate is washed with distilled 15 water and is dried in an oven. The above operation is repeated three more times, with a total of four exchanges with the lanthanum nitrate solution.

The material obtained, after the last exchange, is dried in an oven and then calcined in a muffle at 550°C.

20 A solution is prepared, using 1.38 g of ammonium heptamolybdate, 1.56 g of hexahydrated zinc nitrate and 38 g of demineralized water. 18 g of the previously prepared zeolite containing lanthanum, are impregnated by means of the incipient wetness imbibition technique, with 25 a third of the previous solution, dried at 120°C, impreg-

nated again with a third of the solution, dried again, further impregnated with the remaining volume of the solution, dried and then calcined at 500°C for 4 hours.

A catalyst is obtained with 4.4% by weight of La,
5 4.2% by weight of Mo and 1.6% by weight of Zn.

The material is crushed to granules within the 20-40 mesh range.

EXAMPLE 8

75 g of the same Y-zeolite used in Example 6 and
10 1,500 g of a 2 molar aqueous solution of ammonium nitrate, are charged into a 2 liter glass flask. The suspension is maintained under reflux for 3 hours under stirring; after this period, it is filtered on a vacuum Buckner funnel, dried in an oven and calcined in air at a
15 temperature of 550°C for 5 hours, obtaining a Y-zeolite in acidic form.

25 g of the solid product thus obtained are treated with a solution containing 43.3 g of hexahydrated lanthanum nitrate in 500 g of demineralized water. The solution
20 is maintained under reflux conditions for 4 hours, under stirring. At the end of this period, the solution is filtered, the filtrate is washed with distilled water and dried in an oven. The above operation is repeated three more times, with a total of four exchanges with the lanthanum nitrate solution.

The material obtained after the last exchange, is dried in an oven and then calcined in a muffle at 550°C.

20 g of the calcined product are treated at room temperature with a solution consisting of 160 ml of water 5 and 11.2 g of an aqueous solution of tetra-amine palladium nitrate (Pd 5% max., Alfa Aesar). The whole mixture is stirred for 4 hours, at room temperature. After this period, it is filtered on a Buckner funnel, washed and dried in an oven at 120°C for 16 hours. Calcination is 10 effected at a temperature of 400°C in air for 12 hours.

16 g of the catalyst thus obtained are mixed with 10.81 g of pseudoboehmite VERSAL 250 (UOP) and 64 g of an aqueous solution of acetic acid at 1.5%. The whole mixture is stirred for 30 minutes at room temperature, and 15 is then dried on an heated plate. It is subsequently dried at 120°C for 16 hours and is calcined at 500°C for 4 hours.

A Y-zeolite is obtained, containing 2.1% by weight of La and 1.0% by weight of Pd, bound with alumina, 20 wherein the amount of binder corresponds to about 30% of the total weight of the catalytic composition.

The material is crushed to granules within the 20-40 mesh range.

EXAMPLE 9

25 30 g of the same Y-zeolite used in Example 1 are

charged into a glass flask. A solution is prepared using 2.3 g of ammonium heptamolybdate, 2.6 g of hexahydrated zinc nitrate and 62.4 g of demineralized water. The extruded zeolite is impregnated using the incipient wetness 5 inbibition procedure, with a third of the previous solution, dried at 120°C, impregnated again with a third of the solution, dried again, further impregnated with the remaining volume of the solution, dried and then calcined at 500°C for 4 hours.

10 A catalyst is obtained with 3.8% by weight of Mo and 1.7% by weight of Zn.

The material is crushed to granules within the 20-40 mesh range.

EXAMPLES OF CATALYTIC PERFORMANCES

15 The catalytic activity tests indicated in the following examples were carried out in the experimental equipment and with the operative conditions described hereunder.

Catalytic test: equipment and operative conditions

20 The conversion of hydrocarbon mixtures is carried out in a fixed bed tubular reactor having the following characteristics: material = AISI 316L stainless steel, length 400 mm, internal diameter = 12 mm, external diameter of the internal thermocouple sheath = 3 mm. The reactor is placed in an oven having differential-zone heat- 25

ing, which allows the selected reaction temperature to be reached.

The catalyst used for the test has a particle size of > 10 mesh. The catalyst charge is of 2÷8 g and is 5 placed in the reactor between two layers of granular corundum.

The flow rate of the hydrocarbon mix is regulated by means of an HPLC pump. The hydrogen flow rate is controlled by means of a thermal mass flow meter. The reactor is of the down-flow type. The two feedings are 10 injected and mixed at the inlet of the reactor, in the zone filled with inert material (granular corundum) where the reaction temperature is reached before coming in contact with the catalyst. The plant pressure is controlled 15 through a setting valve at the outlet of the reactor (back pressure valve control). After the pressure setting valve, the stream is sent to a volume flow meter. An aliquot of the gaseous stream is periodically deviated (about every two hours) to an on-line gas chromatograph, 20 for analysis of the products.

In the starting phase of the activity test, the catalyst is heated to the reaction temperature, under a nitrogen stream or, alternatively, a hydrogen stream, at 25 low pressure and for one hour, in order to dry the catalyst and remove air from the reactor. Hydrogen is subse-

quently fed, if nitrogen was used before, and the pressure is increased to the value established for the reaction. The feeding of the hydrocarbon mixture is then started, at the flow rate established for the reaction.

5 The mix of hydrocarbons at the outlet of the reactor is partially cooled before reaching the pressure setting valve, it is then cooled to about 50°C, said temperature being maintained in the whole line to the gas chromatograph. Before reaching the flow volume meter, the gas is
10 cooled to room temperature.

The composition of the hydrocarbon mix in the feeding is established through an out-of-line gas chromatographic analysis, with sample injection in liquid phase.

15 The catalytic performances are evaluated by calculating the conversion of the reagents and the yield of the products on the basis of the gas chromatographic analysis integrated with the process data, such as the inlet and outlet flow rates.

20 The regeneration of the catalyst is effected, when required, after the activity test. Regeneration is carried out in the same reactor used for the reaction. The regeneration operative conditions are the following: temperature = 450÷550°C, pressure = 1÷3 bar, oxygen concentration = 0.1÷20% and GHSV space velocity = 3,000÷6,000
25

hours⁻¹. In particular, the treatment starts with a nitrogen flow, to which an equal air flow is progressively added (in about 1 hour), the nitrogen flow is then progressively reduced to zero (in about 1 hour) and the treatment is prolonged from 5 to 24 hours, in relation to the duration of the previous activity test. At the end of the treatment the reactor is purged with a nitrogen flow and the catalytic activity test can be re-started.

Catalytic test: performances

Examples of catalytic activity follow, using the catalysts whose preparation was described in Examples 1-9.

The results are indicated in the tables which specify the catalyst characteristics, references to the preparation example, the operative conditions and the catalytic performances obtained.

As far as the operative conditions are concerned, it should be pointed out that WHSV means the weight space velocity (Weight Hourly Space Velocity) expressed as kg of hydrocarbons fed/hour/kg of catalyst, and TOS means the working time of the catalyst (Time On Stream), calculated starting from the beginning of the test with fresh catalyst or, in the case of an operating period following a regeneration, from the re-starting of the test with the regenerated catalyst.

The performances are expressed in terms of total conversions of the hydrocarbon (or mix of hydrocarbons) fed and composition of the mix of hydrocarbons at the outlet of the reactor. In particular the concentration of 5 the following products are specified: methane (CH_4), ethane (C_2H_6), propane (C_3H_8), n-butane ($\text{n-C}_4\text{H}_{10}$), isobutane ($\text{i-C}_4\text{H}_{10}$), summation of paraffins with more than 4 carbon atoms ($\Sigma \text{Par. } >\text{C}_4$) and summation of all linear paraffins with the exclusion of methane ($\Sigma \text{n-Par. } >\text{C}_1$).

10 In the following Table 1 (3 examples, from Ex. 10/A to Ex. 10/C) the operative conditions are indicated together with the catalytic performances obtained using a catalyst based on Pd on USY-zeolite, prepared as described in Example 1. In particular, the results shown 15 were obtained under different operative conditions, by varying the reaction temperature between 400 and 450°C and the molar ratio $\text{H}_2/\text{Hydrocarbons}$ between 10.3 and 32.7. The results demonstrate that this catalyst can be advantageously used for the purposes of the present invention.

20 Tables 2-5 (12 examples, from Ex. 11/A to Ex. 14/C) specify the results obtained with catalysts having a composition different from that of Example 10. They are based on Zn/Mo, Zn/Cu, Mo and Zn, all on USY-zeolites; 25 their preparation is described in examples 2-5. Also in

this case, the results were obtained under different operative conditions, with reaction temperatures of 400÷450°C and molar ratio H₂/Hydrocarbons of 9.8÷35.4. The results show that the purposes of the present invention can be achieved with all these catalysts, in a wide composition range.

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20

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Table 1 – EXAMPLES 10/A – 10/C

* Catalyst		Type and Preparation Reference Pd/USY Zeolyst CBV 500; See Ex. 1																																														
Example 10/A																																																
* Operative conditions																																																
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 45%;">Hydrocarbons fed</td><td colspan="7">100% 1,2,4-trimethyl benzene</td></tr> <tr> <td>Reaction temperature (°C)</td><td colspan="7">400</td></tr> <tr> <td>WHSV (hours⁻¹)</td><td colspan="7">0.8</td></tr> <tr> <td>Pressure (bar)</td><td colspan="7">60</td></tr> <tr> <td>H₂/Hydrocarbons molar ratio</td><td colspan="7" rowspan="2">10.3</td></tr> </table>								Hydrocarbons fed	100% 1,2,4-trimethyl benzene							Reaction temperature (°C)	400							WHSV (hours ⁻¹)	0.8							Pressure (bar)	60							H ₂ /Hydrocarbons molar ratio	10.3							
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H ₂ /Hydrocarbons molar ratio	10.3																																															
* Catalytic performances																																																
10	TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)																																													
			CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4																																								
7		100	7.0	16.6	52.2	12.9	9.5	1.8																																								
								82.8																																								
Example 10/B																																																
* Operative conditions																																																
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			CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4																																								
17.5		100	19.9	38.2	39.7	1.2	0.8	0.1																																								
								79.2																																								
Example 10/C																																																
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* Catalytic performances																																																
20	TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)																																													
			CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4																																								
17		100	14.9	25.6	52.9	3.8	2.8	0.0																																								
								82.4																																								

Table 2- EXAMPLES 11/A – 11/C

* Catalyst

Type and Preparation Reference | ZnMo/USY Zeolyst CBV500; See Ex. 2

Example 11/A

* Operative conditions

Hydrocarbons fed	100% 1,2,4-trimethyl benzene
Reaction temperature (°C)	400
WHSV (hours ⁻¹)	0.8
Pressure (bar)	60
H ₂ /Hydrocarbons molar ratio	10.5

* Catalytic performances

TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
7	100	4.8	11.4	48.4	18.5	13.5	3.5	80.3

Example 11/B

* Operative conditions

Hydrocarbons fed	100% 1,2,4-trimethyl benzene
Reaction temperature (°C)	450
WHSV (hours ⁻¹)	0.8
Pressure (bar)	60
H ₂ /Hydrocarbons molar ratio	10.7

* Catalytic performances

TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
17	100	16.1	30.9	49.9	1.8	1.2	0.1	82.7

Example 11/C

* Operative conditions

Hydrocarbons fed	100% 1,2,4-trimethyl benzene
Reaction temperature (°C)	450
WHSV (hours ⁻¹)	0.8
Pressure (bar)	60
H ₂ /Hydrocarbons molar ratio	35.4

* Catalytic performances

TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
17.5	100	14.6	19.9	47.2	10.9	7.0	0.4	78.3

Table 3 EXAMPLES 12/A – 12/C

* Catalyst

Type and Preparation Reference | ZnCu/USY Zeolyst CBV500; See Ex. 3

Example 12/A

* Operative conditions

Hydrocarbons fed | 100% 1,2,4-trimethyl benzene

5 Reaction temperature (°C) | 450

WHSV (hours⁻¹) | 0.8

Pressure (bar) | 60

H₂/Hydrocarbons molar ratio | 9.8

* Catalytic performances

TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)							
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1	
10	17	99.2	4.6	4.5	31.2	14.1	18.7	23.4	57.6

Example 12/B

* Operative conditions

Hydrocarbons fed | 100% 1,2,4-trimethyl benzene

Reaction temperature (°C) | 400

WHSV (hours⁻¹) | 0.8

Pressure (bar) | 60

H₂/Hydrocarbons molar ratio | 32.0

15 * Catalytic performances

TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)							
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1	
15	7	100	2.3	3.9	29.7	21.6	29.8	12.7	63.3

Example 12/C

* Operative conditions

Hydrocarbons fed | 100% 1,2,4-trimethyl benzene

20 Reaction temperature (°C) | 450

WHSV (hours⁻¹) | 0.8

Pressure (bar) | 60

H₂/Hydrocarbons molar ratio | 32.0

* Catalytic performances

TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)							
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1	
25	17	100	6.7	8.8	46.8	19.9	15.1	2.6	77.2

Table 4 EXAMPLES 13/A – 13/C

* Catalyst

Type and Preparation Reference Mo/USY Zeolyst CBV500; See Ex. 4

Example 13/A

* Operative conditions

5	Hydrocarbons fed	100% 1,2,4-trimethyl benzene
	Reaction temperature (°C)	400
	WHSV (hours ⁻¹)	0.8
	Pressure (bar)	60
	H ₂ /Hydrocarbons molar ratio	10.0

* Catalytic performances

10	TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
			CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
	17	100	1.4	9.4	40.1	21.3	18.7	9.0	76.0

Example 13/B

* Operative conditions

15	Hydrocarbons fed	100% 1,2,4-trimethyl benzene
	Reaction temperature (°C)	450
	WHSV (hours ⁻¹)	0.8
	Pressure (bar)	60
	H ₂ /Hydrocarbons molar ratio	10.0

* Catalytic performances

15	TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
			CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
	17	100	6.0	20.7	56.6	8.8	5.8	2.1	87.0

Example 13/C

* Operative conditions

20	Hydrocarbons fed	100% 1,2,4-trimethyl benzene
	Reaction temperature (°C)	450
	WHSV (hours ⁻¹)	0.8
	Pressure (bar)	60
	H ₂ /Hydrocarbons molar ratio	31.9

* Catalytic performances

25	TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
			CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
	17	100	12.9	26.3	47.8	7.7	5.1	0.2	81.9

Table 5 EXAMPLES 14/A – 14/C

* Catalyst								
Type and Preparation Reference	Zn/USY Zeolyst CBV500; See Ex. 5							
Example 14/A								
* Operative conditions								
Hydrocarbons fed	100% 1,2,4-trimethyl benzene							
Reaction temperature (°C)	450							
WHSV (hours ⁻¹)	0.8							
Pressure (bar)	60							
H ₂ /Hydrocarbons molar ratio	10.1							
* Catalytic performances								
TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
17.5	97.4	4.2	4.4	29.1	11.6	14.5	20.3	48.0
Example 14/B								
* Operative conditions								
Hydrocarbons fed	100% 1,2,4-trimethyl benzene							
Reaction temperature (°C)	400							
WHSV (hours ⁻¹)	0.8							
Pressure (bar)	60							
H ₂ /Hydrocarbons molar ratio	32.8							
* Catalytic performances								
TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
7	99.6	1.5	2.2	31.4	21.5	29.1	12.0	59.2
Example 14/C								
* Operative conditions								
Hydrocarbons fed	100% 1,2,4-trimethyl benzene							
Reaction temperature (°C)	450							
WHSV (hours ⁻¹)	0.8							
Pressure (bar)	60							
H ₂ /Hydrocarbons molar ratio	32.3							
* Catalytic performances								
TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
17	99.6	6.1	7.0	50.1	18.5	14.5	3.0	76.5

Table 6 (3 examples, from Ex. 15/A to Ex. 15/C) shows the operative conditions and the catalytic performances obtained using a catalyst based on Pd on USY-zeolite, prepared as described in example 6.

5

Table 6 EXAMPLES 15/A – 15/C

* Catalyst								
Type and Preparation Reference	Pd/USY Tosoh HSZ 320 HOA; See Ex. 6							
Example 15/A								
* Operative conditions								
Hydrocarbons fed	100% 1,2,4-trimethyl benzene							
Reaction temperature (°C)	400							
WHSV (hours ⁻¹)	0.7							
Pressure (bar)	60							
H ₂ /Hydrocarbons molar ratio	10.1							
* Catalytic performances								
Mix composition at the reactor outlet (weight %)								
TOS (hr)	Conv. (%)	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
7	100	7.9	16.0	48.8	14.2	11.0	2.1	79.0
Example 15/B								
* Operative conditions								
Hydrocarbons fed	100% 1,2,4-trimethyl benzene							
Reaction temperature (°C)	450							
WHSV (hours ⁻¹)	0.7							
Pressure (bar)	60							
H ₂ /Hydrocarbons molar ratio	10.1							
* Catalytic performances								
Mix composition at the reactor outlet (weight %)								
TOS (hr)	Conv. (%)	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
17.5	100	17.0	32.4	47.4	1.9	1.3	0.2	81.7
Example 15/C								
* Operative conditions								
Hydrocarbons fed	100% 1,2,4-trimethyl benzene							
Reaction temperature (°C)	450							
WHSV (hours ⁻¹)	0.7							
Pressure (bar)	60							
H ₂ /Hydrocarbons molar ratio	35.7							
* Catalytic performances								
Mix composition at the reactor outlet (weight %)								
TOS (hr)	Conv. (%)	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
17.5	100	11.5	21.2	51.7	9.1	6.5	0.1	82.0

20 25 Table 7 (3 examples, from Ex. 16/A to Ex. 16/C) shows the

operative conditions and the catalytic performances obtained using a catalyst based on Zn/Mo on USY-zeolite previously exchanged with La, prepared as described in Example 7. Also in this case, the results obtained are 5 extremely good and show that it is possible to operate in an advantageous way also using compositions having a more complex composition, as mentioned in the description of the present invention.

Table 8 (2 examples, from Ex. 17/A to Ex. 17/B) 10 shows the results relating to the same catalyst used in Examples 16/A-16/C of Table 7, adopted in a test of a longer duration. The results of Example 17/A were obtained after 260 hours of operation after the last regeneration and it was demonstrated that an excellent catalytic performance is maintained. The results of Example 15 17/B (270 hours after the last regeneration), were obtained after increasing the reaction temperature to 500°C; the yield to light paraffins, particularly ethane and propane, is extremely good and the methane production 20 is reasonably contained.

Table 7 EXAMPLES 16/A – 16/C

* Catalyst

Type and Preparation Reference | Zn-Mo/La-USY Zeolyst CBV500; See Ex. 7

Example 16/A

* Operative conditions

5	Hydrocarbons fed	100% 1,2,4-trimethyl benzene
	Reaction temperature (°C)	400
	WHSV (hours ⁻¹)	0.8
	Pressure (bar)	60
	H ₂ /Hydrocarbons molar ratio	10.1

* Catalytic performances

10	TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
			CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
	7	100	2.7	8.3	41.8	22.1	18.2	6.9	76.4

Example 16/B

* Operative conditions

15	Hydrocarbons fed	100% 1,2,4-trimethyl benzene
	Reaction temperature (°C)	450
	WHSV (hours ⁻¹)	0.8
	Pressure (bar)	60
	H ₂ /Hydrocarbons molar ratio	10.1

* Catalytic performances

15	TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
			CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
	17.5	100	11.4	24.2	56.6	4.3	2.9	0.6	85.5

Example 16/C

* Operative conditions

20	Hydrocarbons fed	100% 1,2,4-trimethyl benzene
	Reaction temperature (°C)	450
	WHSV (hours ⁻¹)	0.8
	Pressure (bar)	60
	H ₂ /Hydrocarbons molar ratio	31.9

* Catalytic performances

25	TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
			CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
	17	100	12.6	18.8	46.6	13.1	8.2	0.7	78.9

Table 8 EXAMPLES 17/A – 17/B

* Catalyst								
Type and Preparation Reference	Zn-Mo/La-USY Zeolyst CBV500; See Ex. 7							
Example 17/A								
* Operative conditions								
Hydrocarbons fed.	100% 1,2,4-trimethyl benzene							
Reaction temperature (°C)	450							
WHSV (hours ⁻¹)	0.8							
Pressure (bar)	60							
H ₂ /Hydrocarbons molar ratio	31.6							
* Catalytic performances								
TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
260	100	6.9	17.7	48.5	15.1	10.1	1.3	81.8
Example 17/B								
* Operative conditions								
Hydrocarbons fed	100% 1,2,4-trimethyl benzene							
Reaction temperature (°C)	500							
WHSV (hours ⁻¹)	0.8							
Pressure (bar)	60							
H ₂ /Hydrocarbons molar ratio	31.7							
* Catalytic performances								
TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
270	100	17.1	33.8	46.1	1.8	1.1	0.0	81.7

Table 9 (Example 18) shows the results obtained with a Pd on an La-USY based catalyst, prepared according to the description in Example 8. The test was carried out with a feed consisting of dicyclopentadiene. The catalyst effectively converted the feed into low molecular weight paraffins.

Table 9 EXAMPLE 18							
* Catalyst							
Type and Preparation Reference	Pd/La-USY Tosoh HSZ 320 HOA; See Ex. 8						
* Operative conditions							
Hydrocarbons fed	100% di-cyclo pentadiene						
Reaction temperature (°C)	450						
WHSV (hours ⁻¹)	0.7						
Pressure (bar)	60						
H ₂ /Hydrocarbons molar ratio	34.8						
* Catalytic performances							
TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)					
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4
17	100	4.3	10.0	39.1	19.7	13.1	13.8
							74.1

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Table 10 (8 examples, from Ex. 19/A to Ex. 19/H) indicates the results obtained with a Pd on USY based catalyst, prepared according to the description in Example 6. The test was carried out by repeatedly changing the feed, as shown in Table 10. 40÷50 working hours were effected with each different feed, and the catalyst was always regenerated before passing to the subsequent feed. The test clearly shows that the catalyst is capable of effectively converting all the hydrocarbons tested and, at the same time, that the catalyst can be repeatedly regenerated.

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Table 10 - Examples 19/A – 19/H

Catalyst										
Type and Preparation Reference			Pd/USY Tosoh HSZ 320 HOA; See Ex. 6							
* Operative conditions										
Reaction temperature (°C)					450					
WHSV (hours ⁻¹)					0.7					
Pressure (bar)					60					
TOS (hr)					17					
* Catalytic performances										
Feed type	Conv. (%)	Mix composition at the reactor outlet (weight %)								
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4			
5	19/A	100	8.6	21.1	63.9	3.6	2.6	0.3	88.7	
	19/B	98.1	1.2	7.9	21.7	11.2	7.7	19.9	42.7	
	19/C	100	0.9	8.4	30.7	18.4	20.6	17.9	66.3	
	19/D	100	2.1	11.3	42.2	20.6	15.9	8.0	77.1	
	19/E	100	12.2	14.5	44.3	16.6	11.7	0.8	75.6	
	19/F	100	10.4	22.1	48.1	11.2	7.9	0.2	81.6	
	19/G	100	2.9	11.2	36.0	23.2	18.1	8.6	73.7	
	19/H	100	5.1	14.3	44.9	19.8	13.2	2.6	80.0	
10	19/A:	hydrocarbon = 100% cumene, H ₂ / Hydrocarbon molar ratio = 10.1								
	19/B:	hydrocarbon = 100% indane, H ₂ / Hydrocarbon molar ratio = 10.3								
	19/C:	hydrocarbon = 100% indane, H ₂ / Hydrocarbon molar ratio = 19.5								
	19/D:	hydrocarbon = 100% indane, H ₂ / Hydrocarbon molar ratio = 31.7								
	19/E:	hydrocarbon = 100% 1,2,4-trimethyl cyclohexane H ₂ / Hydrocarbon molar ratio = 38.3								
	19/F:	hydrocarbon = mix ethyl benzene + xylene isomers, H ₂ / Hydrocarbon molar ratio = 35.0								
	19/G:	hydrocarbon = mix tetramethyl benzene isomers H ₂ / Hydrocarbon molar ratio = 34.8								
	19/H:	hydrocarbon = 85% weight 1,2,4-trimethyl benzene + 15% weight naphthalene H ₂ / Hydrocarbon molar ratio = 36.0								

Table 11 (5 examples, from Ex. 20/A to Ex. 20/E) indicates the results obtained with a catalyst based on Zn

and Mo on USY-zeolite, prepared according to the description in Example 9. The test was carried out by feeding different types of hydrocarbons, as shown in the same Table 11.

5 20÷30 working hours were effected with each hydrocarbon, and the catalyst was always regenerated before passing to the subsequent feed. The test shows that the catalyst is capable of effectively converting all the hydrocarbons fed and that it can be regenerated.

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Table 11 - Examples 20/A – 20/E

Catalyst							
Type and Preparation Reference		ZnMo/USY Zeolyst CBV 500; See Ex. 9					
* Operative conditions							
Reaction temperature (°C)		420					
WHSV (hours ⁻¹)		0.8					
Pressure (bar)		60					
TOS (hr)		11					
* Catalytic performances							
Feed type	Conv. (%)	Mix composition at the reactor outlet (weight %)					
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4
20/A	100	6.4	15.5	57.9	10.9	7.7	1.6
20/B	100	10.3	17.1	55.7	9.6	6.5	0.7
20/C	100	6.4	12.0	42.1	19.2	13.2	7.0
20/D	100	10.4	18.7	53.0	10.1	6.9	0.9
20/E	100	3.4	11.5	44.9	20.5	15.5	4.0
20A: hydrocarbon = 100% decahydronaphthalene (decaline) H ₂ / Hydrocarbon molar ratio = 11.6							
20B: hydrocarbon = 100% n-decane H ₂ / Hydrocarbon molar ratio = 14.3							
20C: hydrocarbon = 100% di-cyclo pentadiene H ₂ / Hydrocarbon molar ratio = 33.5							
20D: hydrocarbon = 100% weight 1,2,4 – trimethyl cyclohexane H ₂ / Hydrocarbon molar ratio = 11.8							
20E: hydrocarbon = 13.5% decahydronaphthalene + 13.1% n-decane + 12.7% di-cyclo pentadiene + 13.4% 1,2,4-trimethyl cyclohexane + 13.1% naphthalene + 34.2% 1,2,4-trimethyl benzene, H ₂ / Hydrocarbon molar ratio = 33.8							

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Table 12 (2 examples, from Ex. 21/A to Ex. 21/B) indicates the results obtained with the feed consisting of two different high molecular weight hydrocarbon mixtures (the composition of the mixtures is specified in the same 5 Table 12). A catalyst based on Zn and Mo on La-USY-zeolite was used in this case (prepared according to the description in Example 9). The results show the conversion obtained with aromatic compounds having more than one benzene ring.

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Table 12 - Examples 21/A – 21/B

Catalyst							
Type and Preparation Reference		ZnMo/USY Zeolyst CBV 500; See Ex. 9					
* Operative conditions							
Reaction temperature (°C)		450					
WHSV (hours ⁻¹)		0.9					
Pressure (bar)		60					
TOS (hr)		for ex. 21/A = 21 h; for Ex. 21/B = 80 h					
* Catalytic performances							
Feed type	Conv. (%)	Mix composition at the reactor outlet (weight %)					
21A	100	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4
21/B	100	5.3	15.7	46.3	18.0	12.3	Σn.Par >C1
21/A:	hydrocarbon = 50% by weight of dimethyl naphthalenes + 50% by weight of trimethyl naphthalenes, H ₂ / Hydrocarbon molar ratio = 39.4						
21/B:	hydrocarbon = 84.5% by weight of 1,2,4-trimethyl benzene + 4.4% by weight of dimethyl naphthalenes + 4.4% by weight of trimethyl naphthalenes + 1.8% by weight of anthracene + 1.7% by weight of di-hydro anthracene + 2.5% by weight of di-hydro phenanthrene + 0.7% by weight of methyl anthracene, H ₂ / Hydrocarbon molar ratio = 30.1						

Table 13 (Example 22) indicates the results obtained in a test of a longer duration with a catalyst based on Zn and Mo on USY-zeolite, prepared according to the description in Example 7. The feed composition was changed several 25 in

times during the test, but the catalyst was never regenerated. The test was interrupted after 1,200 working hours. As indicated in Table 13, the feed contained sulfured compounds with concentrations of 5,000÷6,500 ppm, 5 for long running periods, and the catalytic performance was always excellent for the purposes of the present invention.

Table 14 (Example 23) indicates the results obtained with a catalyst based on Zn and Mo on USY-zeolite, prepared according to the description in Example 7. The test was carried out with a mix of hydrocarbons containing ethyl benzene, xylenes, styrene, methyl styrenes, cumene, trimethyl benzene, methyl ethyl benzenes, indane, di-cyclo pentadiene, naphthalenes and methyl naphthalenes, 10 according to the composition shown in the same Table 14. The test clearly demonstrates that the catalyst is capable of effectively converting the entire hydrocarbon mix 15 fed to low molecular weight paraffins.

Table 13 EXAMPLE 22

* Catalyst											
Type and Preparation Reference				Zn-Mo/La-USY Zeolyst CBV500; See Ex. 7							
* Operative conditions											
Reaction temperature (°C)				450							
WHSV (hours ⁻¹)				0.8							
Pressure (bar)				60							
H ₂ /Hydrocarbons molar ratio				31.9							
* Catalytic performances											
Hydrocarbons fed = 100% 1,2,4-trimethyl benzene											
TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)									
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4				
17	100	8.7	17.4	46.7	15.7	10.3	1.2				
275	100	6.5	16.7	47.2	16.6	11.0	1.6				
479	100	6.3	15.4	45.9	17.7	11.9	2.0				
Hydrocarbons fed = 99.4% 1,2,4-trimethyl benzene + 5000 ppm thio-octanol + 1500 ppm di-benzo thiophene											
TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)									
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4				
526	100	6.9	21.1	55.9	9.2	6.2	0.5				
581	100	7.2	22.9	56.4	7.8	5.3	0.4				
623	100	7.7	22.6	57.0	7.3	5.0	0.4				
Hydrocarbons fed = 69.5% 1,2,4-trimethyl benzene + 30% naphthalene + 5000 ppm di-benzo thiophene											
TOS (hr)	Conv. (%)	Mix composition at the reactor outlet (weight %)									
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4				
625	100	7.8	22.7	56.8	7.3	5.0	0.3				
819	100	6.3	20.7	57.2	8.8	6.1	0.6				
999	100	5.7	19.2	57.3	9.8	6.7	0.8				
1183	100	6.1	16.5	57.1	11.3	7.8	0.9				

Table 14 - Example 23								
Catalyst								
Type and Preparation Reference	ZnMo/La-USY Zeolyst CBV 500; See Ex. 7							
* Operative conditions								
Reaction temperature (°C)	420							
WHSV (hours ⁻¹)	0.8							
Pressure (bar)	60							
H ₂ /Hydrocarbons molar ratio	19.9							
* Catalytic performances								
TOS (h)	Conv. (%)	Mix composition at the reactor outlet (weight %)						
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	I-C ₄ H ₁₀	Σ Par.>C4	Σn.Par >C1
11	100	3.7	16.6	47.5	16.8	11.7	3.2	82.5
Hydrocarbons fed = 5% ethyl benzene + 10% mix of xylenes + 20% styrene + 10% mix of methyl styrenes + 3% cumene + 12% mix of trimethyl benzenes and methyl ethyl benzenes + 10% indane + 25% di-cyclo pentadiene + 5% mix of naphthalenes and methyl naphthalenes								

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